Method of measuring remaining capacity of a storage cell.

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Inventor: FANG WEI-CHOU (US)

Applicant: AMERICAN TELEPHONE & TELEGRAPH (US)

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- EP0146093
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Abstract of **EP0516336**

The remaining capacity of a storage cell, particularly a valve regulated lead-acid cell, is determined by measuring its impedance at typically two or three relatively low frequencies f, e.g, frequencies in the approximate range of 0.01 to 1.0 Hz. In one scheme, the imaginary part Z sec of the complex impedance Z(=Z min + jZ sec) is plotted vs. f<-1/2>, whereby the intercept Z sec _o (at f <-1/2>=0) of the best-fitting straight line of the plot is a measure of the cell's remaining capacity. In another scheme, the slope (dZ sec /dZ min) of a plot of the imaginary part Z sec vs. real part Z min of the complex impedance Z, again as measured at such relatively low frequencies f, is a measure of the cell's remaining capacity.

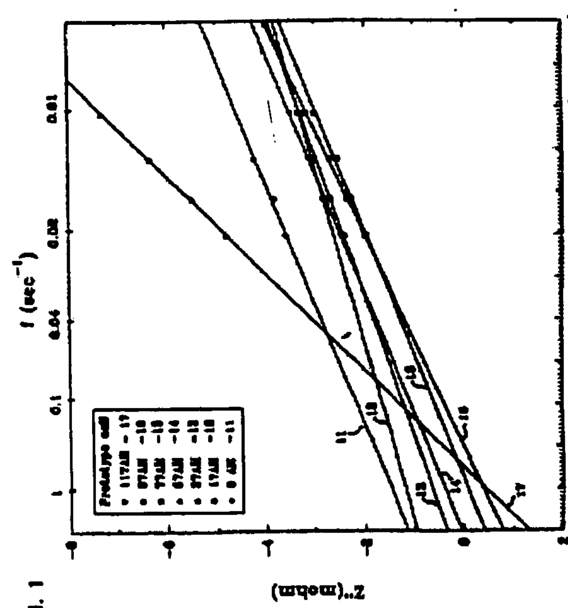

FIG. 1

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(54) **Method of measuring remaining capacity of a storage cell**

Verfahren zur Messung der verbleibenden Ladung einer Speicherzelle

Procédé de mesure de la charge résiduelle d'un élément accumulateur

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(73) Proprietor: **AT&T Corp.**
New York, NY 10013-2412 (US)

(72) Inventor: **Fang, Wei-Chou**
Bridgewater, New Jersey 08807 (US)

(74) Representative:
Buckley, Christopher Simon Thirsk et al
Lucent Technologies (UK) Ltd,
5 Mornington Road
Woodford Green, Essex IG8 0TU (GB)

(56) References cited:
EP-A- 0 146 093 **GB-A- 2 175 700**

- **JOURNAL OF POWER SOURCES vol. 27, no. 4, October 1989, LAUSANNE CH pages 287 - 295,R.T.BARTON ET AL.:'Estimation of the Residual Capacity of Maintenance-Free Lead-Acid Batteries'**
- **REVUE GENERALE DE L'ELECTRICITE no. 3, March 1990, PARIS FR pages 50 - 53;J. ALZIEU ET AL.: 'Un paramètre de controle de l'état d'une batterie d'accumulateurs en service: la résistance électric interne'**
- **CONF. PROC. INTELEC '86 October 1986, TORONTO CA pages 365 - 368 S.DEBARDELABEN:'Determining the End of Battery Life'**

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Description

This invention relates to methods of determining the remaining capacity of a storage cell, such as an electrolyte starved lead-acid cell (also known as "valve regulated" or "sealed" lead-acid cell).

An important measure of the remaining discharge time period t during which a cell can deliver power to an electrical load is the cell's remaining capacity ("reserve capacity") at a constant discharging current I_d. Typically, this remaining capacity is measured in ampere-hours (AH). In turn, it is important to have a remotely located sensing means (connected by wires to the cell) for determining this time period $t=AH/I_d$.

Lead-acid cells generally have the property that, except for a relatively small time interval t_o (approximately between 0.2t and 0.3t) toward the end of this time period t, the terminal voltage V of the cell is approximately constant. Thus the power $P=VI_d$ delivered to the load will be approximately constant except during the relatively small time interval t_o.

In a paper entitled "Internal Resistance: Harbinger of Capacity Loss in Starved Electrolyte Sealed Lead Acid Batteries," published in Intelec 87 Conference Proceedings, pp. 128-131 (1987), and authored by F.J. Vaccaro and P. Casson, a technique for determining the remaining capacity of a valve-regulated lead-acid cell is disclosed. In that technique an alternating voltage at 1 KHz is applied across the terminals of the cell and the impedance is measured and compared with a calibration curve. However, the technique essentially measures only the purely resistive component of the impedance of the electrolyte in the cell and therefore other relevant parameters--which depend on the history of the cell's charging and discharging, heating and cooling, etc.--cannot be detected. Thus the only detectable failure mechanisms are loss of water--other failure mechanisms relevant to remaining capacity are not detected. In particular, the technique does not detect aging, or flaking of electrodes, or insufficient organic additive, or irreversible formation of lead sulfate, all of which depend upon the history of the cell and which deteriorate the condition of the cell, and thus reduce the actually remaining capacity of the cell, but undesirably are not detected by the technique.

In U.S. Patent No. 4,952,862 a technique for predicting the remaining discharge time of a lead-acid storage cell for a given current is disclosed. That technique, however, requires a significant discharge of the cell to make a measurement. Such a discharge can be undesirable because of the consequent deterioration of the cell simply as a result of this required significant discharge.

EP-A-0146093 discloses a process for measurement of the state of discharge of a battery, comprising measuring a first internal impedance of the battery at a first frequency and a second internal impedance of the battery at a second frequency, and then determining the phase angle of the difference between the internal impedances, the phase angle being representative of the state of discharge of the battery.

It is desirable to have a technique for measuring the remaining capacity of a storage cell that mitigates the shortcomings of prior art.

According to one aspect of this invention there is provided a method as claimed in claim 1.

According to another aspect of this invention there is provided a method as claimed in claim 2.

The invention will now be described with reference to the accompanying drawings, in which:

FIG. 1 shows a family of best-fitting straight-line curves of the imaginary part Z", of the complex a-c impedance Z of a specific (prototype) cell versus $f^{-1/2}$, the reciprocal of the square root of the frequency, each such curve being fitted to a plot corresponding to a fixed different remaining capacity (AH) of the cell;

FIG. 2 shows a plot of intercept $Z_o^"$ (obtained from FIG. 1) versus remaining cell capacity (AH) for the specific cell, together with a best-fitting straight line for this plot; and

FIG. 3 shows plots of intercepts $Z_o^"$ versus remaining cell capacities for six different cells, together with a best-fitting straight line for these plots.

Detailed Description

Referring now to the drawings, FIG. 1 shows a set of seven best-fitting straight lines 11, 12, ... 17 for the plots of negative imaginary part (-Z") of the complex impedance Z=Z'+ jZ" vs. $f^{-1/2}$ of a specific VRLA test cell with a specific history. This test cell, for example, is a specific prototype cell, built in the laboratory to simulate the construction of a commercially manufactured LA cell ("production cell"). Each plot is for a given state of remaining charge--i.e., remaining capacity (AH)--of this prototype cell; and each point of the plot is obtained, for example, with the aid of a d-c biased, small a-c amplitude (typically 1 to 5 mV) Kelvin bridge while the cell is otherwise floating (i.e., while there are no other voltages applied to the cell), as known in the art. During and between all these measurements of Z, substantially no discharging of the cell will, or is allowed to, occur. The frequencies f at which the impedances Z are measured for all states of remaining charge, advantageously are all confined within a common frequency range (Δf_1), typically the approximate range of 0.01 Hz to 0.02 Hz, corresponding to $f^{-1/2}$ being within the approximate range of 10 to 7 sec $^{-1/2}$ and to periods T = 1/f being within the approximate range of 50 to 100 seconds.

In any event, the common frequency range (Δf_1) is selected so that all plots are substantially linear. Note that owing to the substantially (nearly) straight-line characteristic of all plots within this common range of frequencies (Δf_1), for each state of charge only two or three

points need to be measured to determine a best-fitting straight line 11, 12,...17 for each such nearly straight line and thus to determine its intercept Z^{*}_{o}.

It should be noted parenthetically here that all cells having the same geometrical and chemical construction as that of the prototype cell will be characterized by a substantial linearity of Z^{*} vs. $f^{-1/2}$ for all frequencies within the common range (Δf_1). This common linearity property makes the invention more useful, as this common frequency range (Δf_1) can later be used for determining a best-fitting straight line for Z^{*} vs. $f^{-1/2}$ and hence of Z^{*}_{o} of a cell of unknown remaining capacity (to be measured)--i.e., taking measurements of Z of each such unknown cell at only two or three frequencies within this common range.

For each of the seven states of remaining charge (AH) of the prototype cell--and hence for each of the seven values of Z^{*}_{o} for the best-fitting straight lines 11, 12,... 17, respectively--the remaining capacity AH, at a discharging current I_d = 10 amp, is measured by a known discharging technique. Then each of the seven values of Z^{*}_{o} is plotted (as Cartesian ordinate) against each of the measured corresponding seven values of AH (as abscissa), whereby points 21, 22,... 27 are plotted, as shown in FIG. 2.

For example, suppose the cell is in such a state of charge that it yields best-fitting straight-line 16 (FIG. 1)--i.e., with intercept Z^{*}_{o} approximately equal to +0.79 milli-ohm. Then suppose further that the remaining capacity of the cell (AH) is measured to be approximately equal to be approximately equal to 97 amp-hours (as measured by means of discharging the cell at the discharging current I_d = 10 amp) until a cut-off voltage of 1.75 V is reached). Accordingly, point 26 (FIG. 2) is plotted with its abscissa equal to 97 AH and its ordinate equal to +0.79 milli-ohm. Similarly, the other points 21, 22, ... 27 are plotted. Note that each of the points 21, 22, ... 27 (in FIG. 2) is labelled with a reference numeral which is equal to the reference numeral for the corresponding best-fitting straight line 11, 12, ... 17 (FIG. 1), respectively, plus ten. Note also that the points 21, 22,... 27 fall roughly along a straight line. Best-fitting straight line 20 is then determined for these points.

In particular, in FIG. 1 the best-fitting straight lines 11, 12, 13, ... 17, respectively, correspond to remaining charge capacities AH (at I_d = 10 amp) that are measured to be approximately equal to 0.0 AH, 17 AH, 37 AH, 57 AH, 77 AH, 97 AH, 117 AH, for the specific prototype cell (for the discharging current I_d = 10 amp). Accordingly, the abscissas for points 21, 22,... 27 in FIG. 2 are equal to these respective values.

Generally, the precise slope and intercept of the best-fitting straight line 20 (FIG. 2) depends somewhat on the history of the prototype cell and perhaps other factors. However, for practical purposes, in accordance with one aspect of the invention, the line 20 is approximately valid for the cell regardless of its history. Indeed, for all cells having the same (geometric and chemical) construction as that of the prototype cell that was used to obtain the best-fitting straight line 20, the line 20 will still be approximately valid, so that this line 20 can be used as a (straight-line) calibration curve for all cells that have the same (geometric and chemical) construction as that of the prototype cell.

Summarizing, for any cell having an unknown remaining charge capacity, but having the same construction as that of the prototype cell and having any history, the best-fitting straight line for a plot of its imaginary part Z^{*} of impedance Z versus $f^{-1/2}$ is determined (without any substantial discharging of the cell), using a d-c biased Kelvin bridge in conjunction with test frequencies within the common frequency range (Δf_1) as that within which the plots (FIG. 1) for the test cell formed substantially straight lines; the intercept Z^{*}_{o} of the best-fitting straight line is measured by extrapolation of this line to $f^{-1/2}=0$; and then the remaining capacity (AH) of the cell can be determined (e.g., by inspection) from the abscissa of the straight line 20 (FIG. 2) corresponding to this value of the intercept Z^{*}_{o}. Note that, since the plot of Z^{*} vs. $f^{-1/2}$ for the cell of unknown remaining charge capacity within the common frequency range (Δf_1) will approximate a straight line, only two or three points need be plotted (provided the test frequencies are confined to this range).

Alternatively, as indicated in FIG. 3, the intercepts Z^{*}_{o} for say six different cells-all having the same constructions but different histories, one of them being the prototype cell--are plotted versus (biased-Kelvin-bridge-measured) remaining capacity (AH), at I_d = 10 amp. All these plotted points tend to cluster along a single straight line. Thus, a best-fitting straight line 30 (FIG. 3) yields a more nearly universal (weighted-average) straight-line calibration curve for determining the remaining capacity of any VRLA cell having the same construction as that of the six cells. For example, if the intercept Z^{*}_{o} is measured to be equal to +1.0, then from the line 30 in FIG. 3, the remaining capacity AH is seen to be equal to approximately 112 amp-hour, again at a discharging current I_d=10 amp.

Note that the slope and intercept of the straight line 20 (FIG. 2) are approximately respectively equal to those of the straight line 30 (FIG. 3). Note also that, except for the prototype cell, all the other six cells plotted in FIG. 3 represent commercially manufactured ("production") cells, with one of them having been "rejected" because it had a significantly higher internal resistance than the other production cells, and another of them being called "dried out" because it had lost 12.9 per centum by weight of its electrolyte.

It should be understood that the common frequency ranges (Δf_1) and (Δf_2) for VRLA cells, within which the plot of Z^{*} vs. $f^{-1/2}$ (FIG. 1) is substantially linear can depend on the geometric and chemical construction of the cell.

Although this invention has been described in detail with reference to specific embodiments, various modifi-

cations can be made. For example, instead of VRLA cells, any lead-acid or other types of electrical storage cells can be used. Instead of best-fitting straight line calibration curves 20, 30, other forms (shapes) of calibration curves can be determined and used to measure the remaining capacity of unknown cells. Instead of using a prototype cell for determining calibration curve 20, a production cell can be used.

Claims

1. A method of determining the remaining capacity of a storage cell, comprising the steps of:

   measuring a first impedance of the cell at a first frequency in an approximate range of 0.001 to 1.0Hz,
   measuring a second impedance of the cell at a second frequency in the approximate range, different from the first frequency,
   determining the intercept, where the reciprocal of the square root of frequency ($f^{-1/2}$) is equal to zero, of a line through a plot of the imaginary part (Z") of the first and second impedances versus the reciprocals of the square roots of the first and second frequencies, respectively.

2. A method of determining the remaining capacity of a storage cell, comprising the steps of:

   measuring at least three impedances of the cell, each at different frequencies in an approximate range of 0.001 to 1.0Hz,
   determining the intercept, where the reciprocal of the square root of frequency ($f^{-1/2}$) is equal to zero, of a best-fit line through a plot of the imaginary part (Z") of the measured impedances versus the reciprocals of the square roots of the respective frequencies at which the impedances were measured.

3. A method as claimed in claim 1 or 2 wherein the cell is a lead-acid storage cell.

4. A method as claimed in claim 1 or 2 wherein the cell is a valve-regulated lead-acid storage cell.

5. A method as claimed in claim 1 or 2 wherein the approximate frequency range is 0.001 to 0.10Hz.

Patentansprüche

1. Verfahren zur Feststellung der verbleibenden Kapazität oder Ladung einer Speicherzelle, umfassend die Schritte des:

   Messens einer ersten Impedanz der Zelle bei einer ersten Frequenz in einem ungefähren Bereich von 0,001 bis 1,0 Hz,
   Messens einer zweiten Impedanz der Zelle bei einer zweiten Frequenz in dem ungefähren Bereich, die von der ersten Frequenz verschieden ist,
   Bestimmens des Schnittpunktes von einer Linie durch eine graphische Darstellung des Imaginärteils (Z") der ersten und der zweiten Impedanz als Funktion der Kehrwerte der Quadratwurzeln der ersten bzw. zweiten Frequenz, bei welchem der Kehrwert der Quadratwurzel der Frequenz ($f^{-1/2}$) = 0 ist.

2. Verfahren zur Feststellung der verbleibenden Kapazität oder Ladung einer Speicherzelle umfassend die Schritte des:
   Messens von wenigstens drei Impedanzen der Zelle, die jede bei einer verschiedenen Frequenz in einem ungefähren Bereich von 0,001 bis 1,0 Hz gemessen wird, Feststellens des Schnittpunkts von einer bestangepaßten Linie durch eine graphische Darstellung des Imaginärteils (Z") der gemessenen Impedanzen als Funktion der Kehrwerte der Quadratwurzeln der jeweiligen Frequenzen, bei welchen die Impedanzen gemessen wurden, bei welchem der Kehrwert der Quadratwurzel der Frequenz ($f^{-1/2}$) = 0 ist.

3. Verfahren nach Anspruch 1 oder 2, bei welchem die Zelle eine Bleisäurespeicherzelle ist.

4. Verfahren nach Anspruch 1 oder 2, bei welchem die Zelle eine ventilregulierte Bleisäurespeicherzelle ist.

5. Verfahren nach Anspruch 1 oder 2, bei welchem der ungefähre Frequenzbereich von 0,001 bis 0,10 Hz beträgt.

Revendications

1. Procédé de détermination de la capacité résiduelle d'un élément d'accumulateur, comprenant les étapes consistant à :

   mesurer une première impédance de l'élément à une première fréquence dans l'intervalle approximatif de 0,001 à 1,0 Hz ;
   mesurer une seconde impédance de l'élément pour une seconde fréquence dans l'intervalle approximatif, différente de la première fréquence ;
   déterminer l'ordonnée à l'origine, pour laquelle l'inverse de la racine carrée de la fréquence ($f^{-1/2}$) est égal à zéro, d'une ligne par le tracé

de la partie imaginaire (Z") de la première et de la seconde impédances en fonction des inverses des racines carrées de la première et de la seconde fréquences, respectivement.

2. Procédé de détermination de la capacité résiduelle d'un élément d'accumulateur, comprenant les étapes consistant à :

mesurer au moins trois impédances de l'élément, chacune pour des fréquences différentes dans l'intervalle approximatif de 0,001 à 1,0 Hz ;

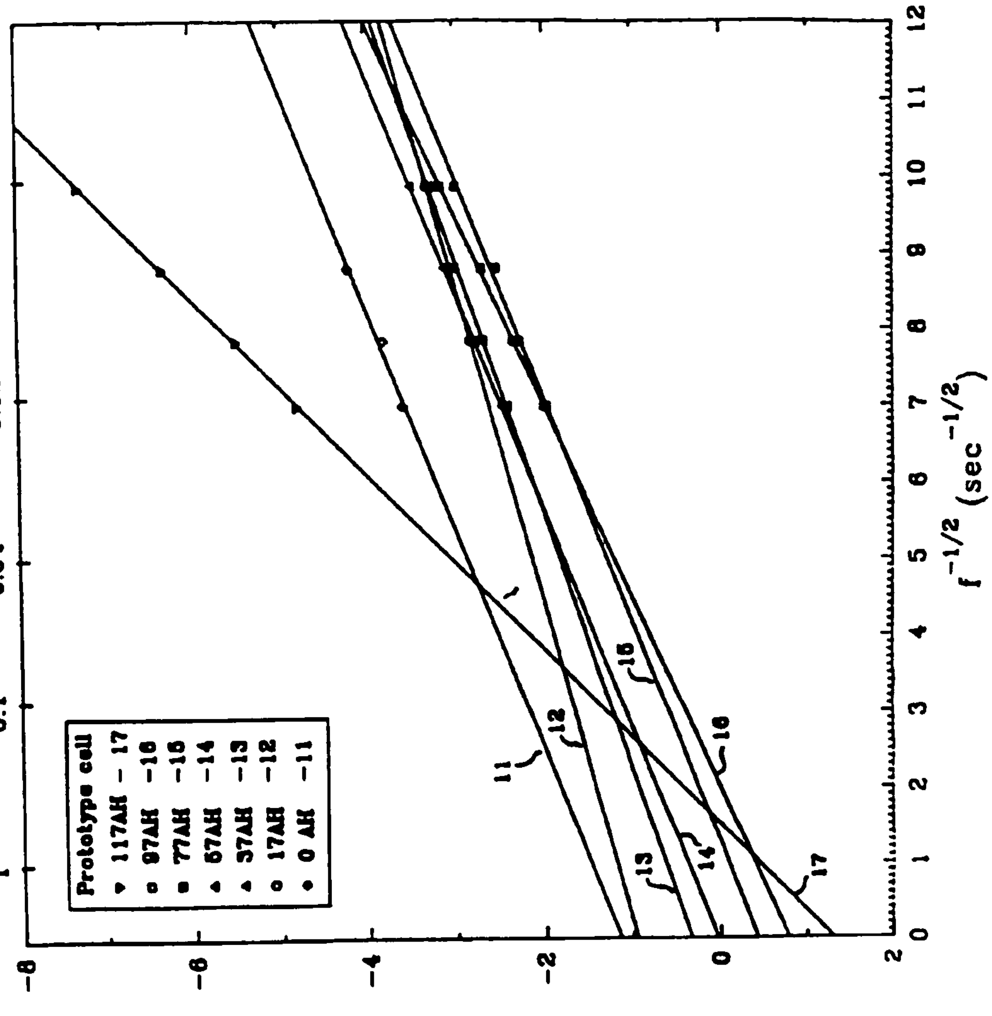
déterminer l'ordonnée à l'origine, pour laquelle l'inverse de la racine carrée de la fréquence ($f^{-1/2}$) est égal à zéro, une ligne s'ajustant le mieux par une courbe de la partie imaginaire (Z") des impédances mesurées en fonction des inverses des racines carrées des fréquences respectives auxquelles les impédances ont été mesurées.

3. Procédé selon les revendications 1 ou 2, dans laquelle l'élément est un élément d'accumulateur plomb-acide régulé par valve.

4. Méthode selon les revendications 1 ou 2, dans laquelle l'élément est un élément d'accumulateur plomb-acide régulé par valve.

5. Méthode selon les revendications 1 ou 2, dans laquelle l'intervalle approximatif de fréquences va de 0,001 à 0,10 Hz.

FIG. 1


f (sec^-1)
Z''(mohm)
f^-1/2 (sec^-1/2)
Prototype cell
117AH - 17
97AH -16
77AH -15
57AH -14
37AH -13
17AH -12
0 AH -11

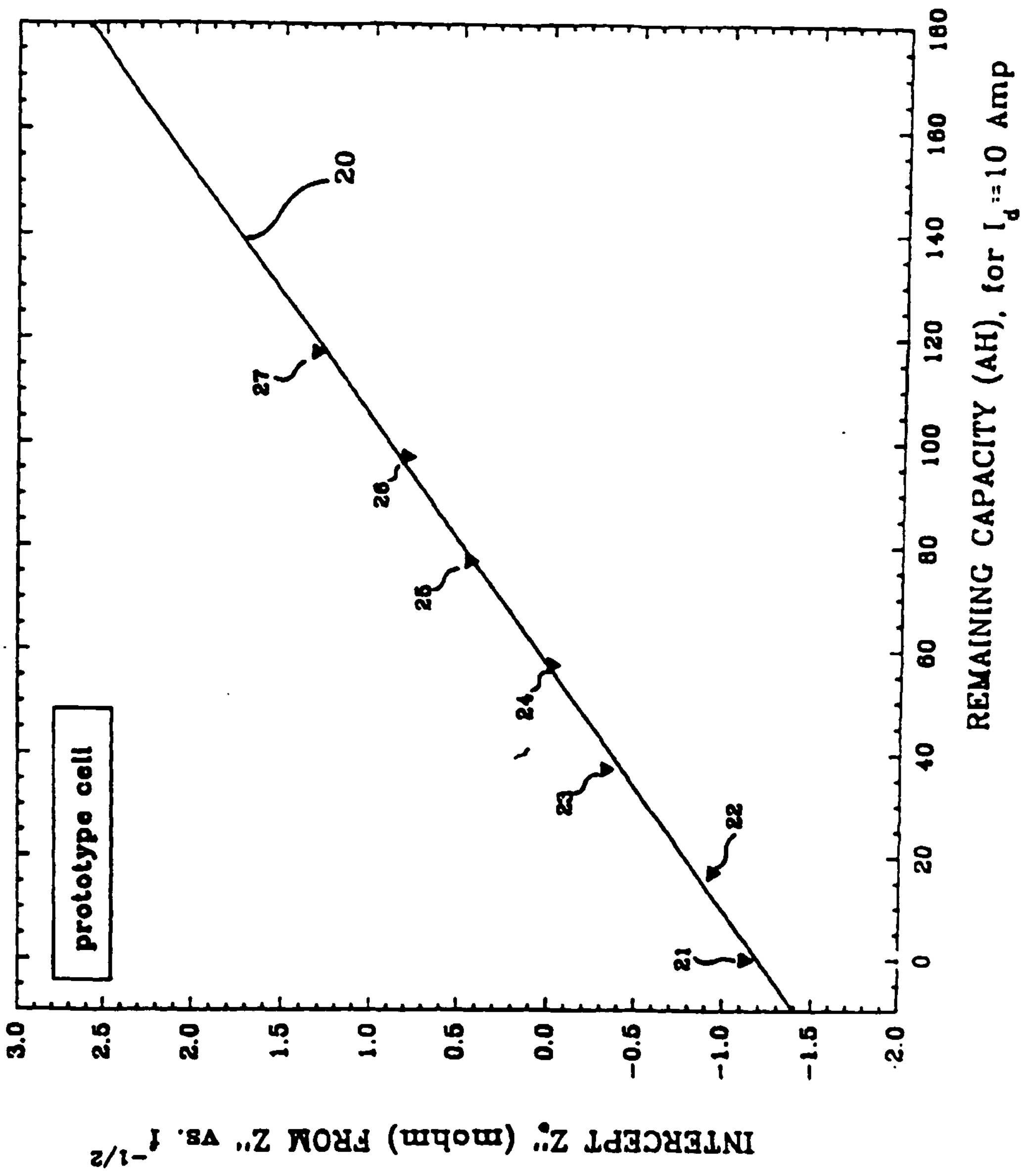
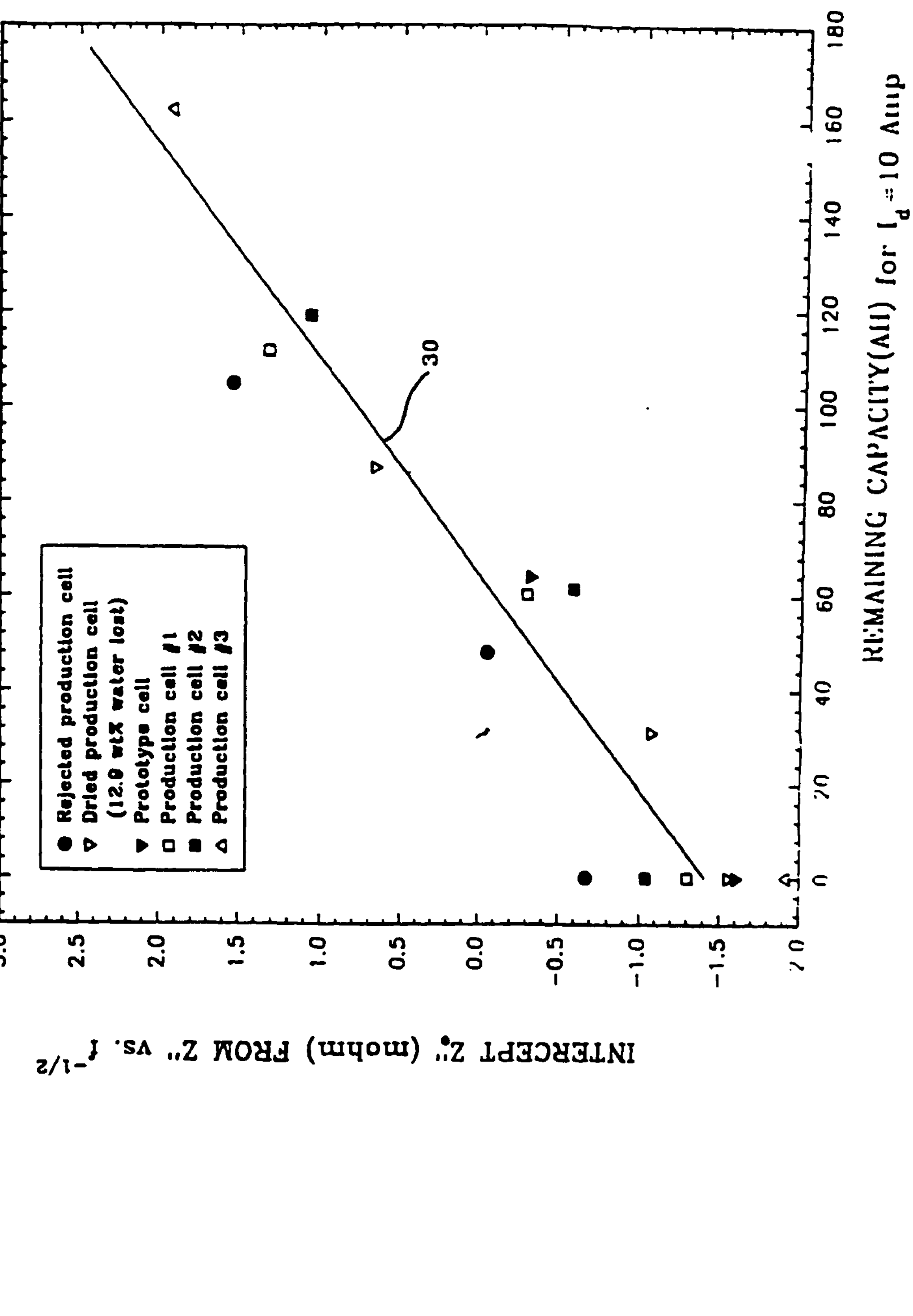

prototype cell
20
21
22
23
24
25
26
27
REMAINING CAPACITY (AH), for I_d=10 Amp
INTERCEPT Z'' (mohm) FROM Z'' vs. f^-1/2
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
0
20
40
60
80
100
120
140
160
180

FIG. 2



Rejected production cell
Dried production cell (12.9 wt% water lost)
Prototype cell
Production cell #1
Production cell #2
Production cell #3
30
REMAINING CAPACITY(AH) for I_d =10 Amp
0
20
40
60
80
100
120
140
160
180
INTERCEPT Z'' (mohm) FROM Z'' vs. f^-1/2
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0

FIG. 3